

# Development of High Conductivity Lithium-ion Electrolytes for Low Temperature Cell Applications

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## Introduction

NASA has continued interest in developing power sources which are capable of operating at low temperatures ( $-20^{\circ}\text{C}$  and below) to enable future missions, such as the Mars Rover and Lander. Thus, under a program sponsored by the Mars Exploration Program, we have been involved in developing Li-ion batteries with improved low temperature performance. To accomplish this task, the focus of the research has been upon the development of advanced electrolyte systems with improved low temperature properties. This had led to the identification of a carbonate-based electrolyte, consisting of 1.0 M  $\text{LiPF}_6$  in EC + DEC + DMC (33:33:34), which has been shown to have excellent performance at  $-20^{\circ}\text{C}$  in Li-ion AA-size prototype cells.(1,2) Other groups are also actively engaged in developing electrolytes which can result in improved low temperature performance of Li-ion cells, including Polystor (3), Yardney, and Covalent. (4)

In addition to developing cells capable of operation at  $-20^{\circ}\text{C}$ , there is continued interest in systems which can successfully operate at even lower temperatures ( $< -30^{\circ}\text{C}$ ) and at high discharge rates ( $> \text{C}/2$ ). Thus, we are currently focusing upon developing advanced electrolytes which are highly conductive at low temperatures and will result in cells capable of operation at  $-40^{\circ}\text{C}$ . One approach to improve the low temperature conductivity of ethylene carbonate-based electrolytes involves adding co-solvents which will decrease the viscosity and extend the liquid range. Candidate solvent additives include formates, acetates, cyclic and aliphatic ethers, lactones, as well as other carbonates. Using this approach, we have prepared a number of electrolytes which contain methyl formate (MF), methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP), and 1,2-dimethoxyethane (DME), some of which have been characterized

and reported earlier.(5) Other groups have also reported electrolytes based on mixtures of carbonates and acetates.(6) In the present study, electrolytes which have been identified to have good low temperature conductivity and stability were incorporated into lithium-graphite cells for evaluation. Using various electrochemical methods, including ac impedance and DC micropolarization techniques, the film formation characteristics of graphite electrodes in contact with various electrolyte formulations was investigated.

## Experimental

The specific conductivity of a number of electrolyte solutions was measured over the temperature range of  $-60^{\circ}\text{C}$  to  $25^{\circ}\text{C}$  using a conductivity cell which consists of two platinized platinum electrodes which are immobilized in a glass apparatus and separated by a fixed distance. The cell constant of the apparatus was determined by comparing the resistivity of a 0.1M KCl solution with the value reported in the literature. The temperature was controlled in these experiments by utilizing a Tenney environmental low temperature chamber ( $\pm 1^{\circ}\text{C}$ ).

Half-cell studies were carried out using O-ring-sealed, glass cells which contained jelly rolls of graphite (KS44) and  $\text{LiCoO}_2$  (Alfa) electrodes with porous polypropylene separator (Celgard 2500) and Li reference electrodes. All electrolyte were of battery-grade purity. Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat (and Solartron 1255 Frequency Response Analyzer for impedance measurements) interfaced with an IBM PC, using Softcorr 352 (and M388 for impedance) software. Cycling Data were collected using an Arbin battery test system.

## Results and Discussion

### Conductivity Measurements

A number of EC-based electrolytes containing low viscosity aliphatic and cyclic esters have been prepared and the conductivity measured over a temperature range of  $-60^{\circ}\text{C}$  to  $25^{\circ}\text{C}$ . The electrolytes assessed consisted of baseline formulations,  $1.0\text{M LiPF}_6$  EC + DEC + DMC (1:1:1), to which low viscosity solvents were added, including: methyl acetate, ethyl acetate, ethyl butyrate, ethyl propionate, and methyl formate. Of the electrolytes investigated, the formulations that displayed the highest conductivity at low temperatures were ones with lower molecular weight acetates and displayed the following trend:  $> 1.0\text{M LiPF}_6$  EC + DEC + DMC + MA (1:1:1:1)  $> 1.0\text{M LiPF}_6$  EC + DEC + DMC + EA (1:1:1:1)  $> 1.0\text{M LiPF}_6$  EC + DEC + DMC + EP (1:1:1:1). The conductivity values for these solutions is shown in Fig. 1.

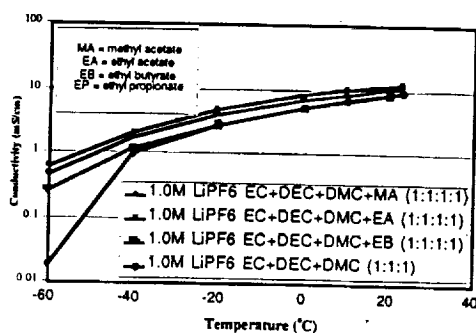


Fig. 1. The effect of low viscosity additives upon the low temperature conductivity of EC-based electrolyte solutions.

In addition to investigating low viscosity additives, we have initiated research into the effect of salt type and salt concentration upon the conductivity of electrolyte solutions at low temperature. It was determined that solutions consisting of  $0.75\text{M LiPF}_6$  EC + DEC + DMC (1:1:1) showed an improvement in conductivity at temperatures below  $-20^{\circ}\text{C}$  compared with  $1.0\text{M LiPF}_6$  EC + DEC + DMC (1:1:1). In addition, the electrolyte formulation  $0.5\text{M LiPF}_6$  EC + DEC + DMC + MA (1:1:1:1) displayed better conductivity at low temperatures below  $-40^{\circ}\text{C}$  compared with the  $1.0\text{M EC} + \text{DEC} + \text{DMC} + \text{MA}$  (1:1:1:1) solution, with little loss in the room temperature values ( $> 10\text{ mS/cm}$  @  $23^{\circ}\text{C}$ ). This electrolyte

solution is a good candidate for ultra-low temperature applications, due to the fact that the conductivity was observed to have greater than  $1\text{ mS/cm}$  at  $-60^{\circ}\text{C}$ . We also initiated investigations into the effect of mixed salt solutions upon the low temperature conductivity and compared  $1.0\text{M LiPF}_6$  solutions with  $0.50\text{M LiPF}_6 + 0.50\text{M LiAsF}_6$  solutions, although little benefit was observed when the conductivity was measured at low temperatures.

### Lithium-Graphite Half-Cells

A number of lithium-graphite cells have been fabricated to study the effect of different electrolytes upon the film formation characteristics on graphite electrolytes and the irreversible and reversible capacities of graphite electrodes. The lithium-graphite half-cells can serve as an additional screening test to identify the compatibility and stability of candidate electrolytes with carbonaceous electrodes. The electrolytes selected in the first group of cells include:  $0.75\text{M LiPF}_6$  EC + DEC + DMC (1:1:1),  $0.75\text{M LiPF}_6$  EC + DEC (30:70),  $0.75\text{M LiPF}_6$  EC + DMC (30:70),  $0.75\text{M LiPF}_6$  EC + DEC + DMC + MA (1:1:1:1), and  $0.75\text{M LiPF}_6$  EC + DEC + DMC + EA (1:1:1:1), and  $0.75\text{M LiPF}_6$  EC + DEC + DMC + DME (1:1:1:1).

As shown in Fig. 3., electrolytes based upon the addition of aliphatic esters, such as methyl acetate and ethyl acetate, were observed to have small irreversible capacities (5th cycle). This suggests that desirable protective interfacial films are formed on the electrode surface with these electrolytes. The exclusively carbonate-based electrolytes showed similar behavior, with higher DMC content resulting in more protective surface films. In contrast, the electrolyte with DME showed the highest irreversible and lowest reversible capacity, suggesting that the solvent is more reactive with the lithiated carbon and/or the electrolyte salt and forms less desirable surface films. Overall, the reversible capacities obtained for the lithium-graphite cells studied, as shown in Fig. 4, were somewhat lower than that observed in experimental and prototype  $\text{LiCoO}_2$ -graphite cells which can be attributed to the selected charge voltage ( $0.025\text{ V vs Li/Li}^+$ ) and the cell design which has excess electrolyte. Some correlation between the extent of irreversible capacity lost in the first cycle and how quickly the cell reflects potentials indicative of the lithium intercalation reaction ( $>150\text{ mV vs. Li/Li}^+$ ) was observed as shown in Fig. 3.

Electrolyte Formulation	Rev Cap 1st Cyc.	Ir Cap 1st Cyc.	Rev Cap 5th Cyc.	Ir Cap 5th Cyc.
0.75M LiPF <sub>6</sub> EC+DMC+DEC (1:1:1)	227.2	106.0	240.4	127.1
0.75M LiPF <sub>6</sub> EC + DMC (30:70)	302.0	94.3	312.6	122.9
0.75M LiPF <sub>6</sub> EC + DEC (30:70)	268.1	106.6	275.4	136.9
0.75M LiPF <sub>6</sub> EC + DMC + DEC + MA (1:1:1:1)	201.5	36.9	236.5	56.9
0.75M LiPF <sub>6</sub> EC + DMC + DEC + EA (1:1:1:1)	210.4	49.9	214.2	68.5
0.75M LiPF <sub>6</sub> EC + DMC + DEC +DME (1:1:1:1)	147.5	138.2	188.3	192.3

Fig. 2. Reversible and irreversible capacities of lithium-graphite cells possessing different EC-based electrolyte formulations.

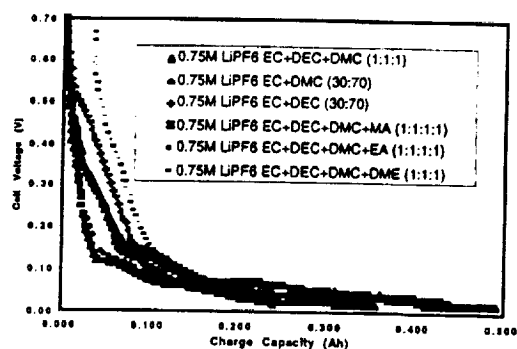


Fig. 3 First lithium intercalation cycle of lithium-graphite cells possessing different EC-based electrolyte formulations.

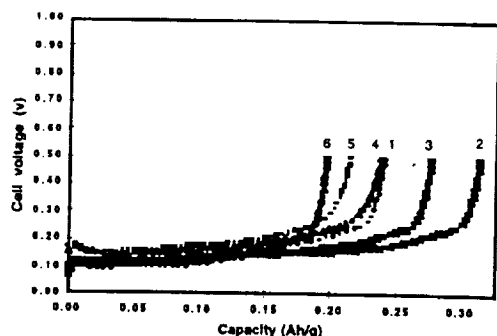


Fig. 4. Reversible capacity (Ah/g) of lithium-graphite cells possessing different EC-based electrolyte formulations (1= EC + DEC + DMC, 2= EC + DMC, 3=EC + DEC, 4= EC + DEC + DMC + MA, 5= EC + DEC + DMC + EA, 6= EC + DEC + DME).

### AC Impedance Measurements

In addition to studying the charge/discharge characteristics of these cells, a.c. impedance was used to probe the interfacial properties of the anode passivating films on the graphite electrodes. As shown in Fig. 5, the carbonate based electrolytes with high DMC content result in cells with lower charge transfer resistance compared with DEC rich electrolytes.

Electrolytes incorporating acetate additives, such as MA or EA show similar behavior to the ternary carbonate mixture, as shown in Fig. 6. Whereas, the electrolyte possessing DME displayed the largest film resistance consistent with the high irreversible capacity observed with this cell. The ac impedance measurements were repeated after the cells had been subjected to a number of cycles and a self-discharge study, as shown in Figs. 7 -8. In the case of the solely carbonate-based electrolytes, little variation was observed in the Nyquist plots generated. However, a dramatic increase in the overall cell resistance and the charge transfer resistance was observed with cells possessing electrolytes with MA or EA, as shown in Fig. 7. These results suggest that these electrolytes continue to react with the lithiated carbon electrode and/or other *in situ* generated byproducts after the initial "formation" cycles. The impact of temperature upon the film resistance was also investigated for all of the samples and displayed similar behavior to that shown in Fig.9.

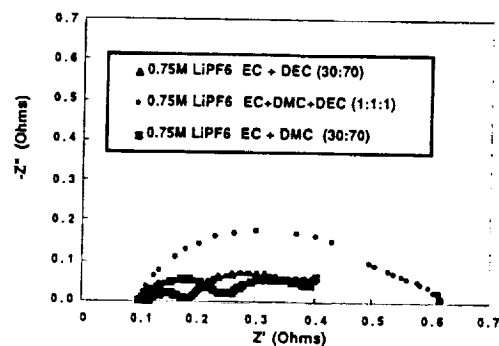


Fig. 5. AC impedance (Nyquist) plots of lithium-graphite cells possessing carbonate-based electrolytes after formation cycles.

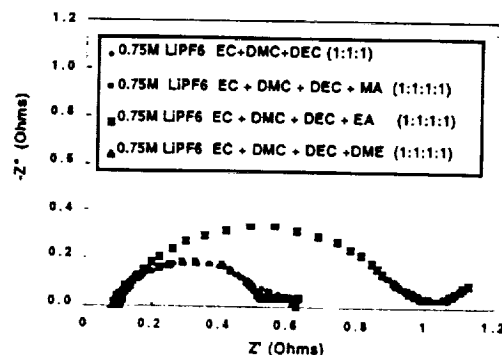


Fig. 6. AC impedance (Nyquist) plots of lithium-graphite cells possessing carbonate-based electrolytes with different low viscosity additives, MA, EA, and DME, after formation cycles.

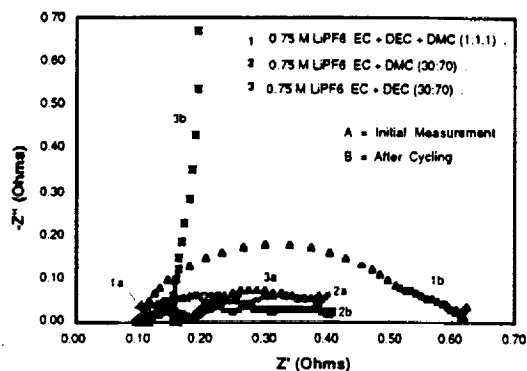


Fig. 7. AC impedance (Nyquist) plots of lithium-graphite cells possessing carbonate-based electrolytes before and after cycling.

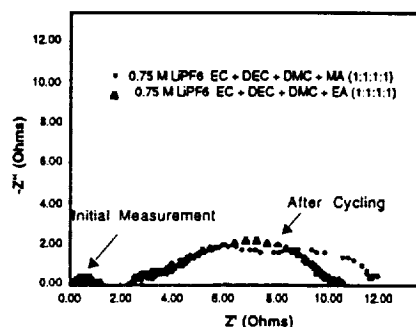


Fig. 8. AC impedance (Nyquist) plots of lithium-graphite cells possessing carbonate-based electrolytes with different low viscosity additives, MA and EA, before and after cycling.

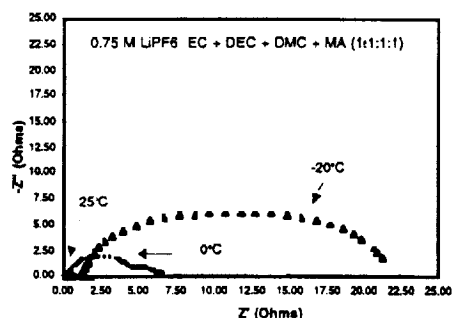


Fig. 9. AC impedance (Nyquist) plots of a lithium-graphite cell possessing EC+DEC+DMC+MA electrolyte at various temperatures.

#### DC Micropolarization Measurements

DC micropolarization techniques were also employed to study the charge transfer behavior of the passivating films on the graphite electrodes at various temperatures. The polarization resistance of the electrodes was calculated from the slopes of the linear plots generated under potentiodynamic conditions at scan rates of 0.02 mV/s. As shown in

Fig. 10 and 11, the cells that had electrolytes which resulted in higher irreversible capacity losses, such as DME and DEC, displayed the lowest polarization resistance. The improved kinetics of Li intercalation observed with these cells may be due to the production of porous, non-protective films which facilitate Li ion diffusion and/or charge transfer. In contrast, the cells containing electrolytes with MA or EA produced films which resulted in high polarization resistance of the electrode. This is undesirable for low temperature applications where the effect is magnified and high rates become difficult to sustain.

The limiting current densities were also determined for the lithium deintercalation process from the graphite electrodes by conducting Tafel polarization measurements to evaluate the rate capability of the electrodes in contact with the various electrolytes. The results obtained correlate well with the DC micro-polarization measurements in that the cells possessing high polarization resistance, i.e. with electrolytes possessing MA or EA, have lower diffusion limiting currents (measured at an overpotential of 250 mV).

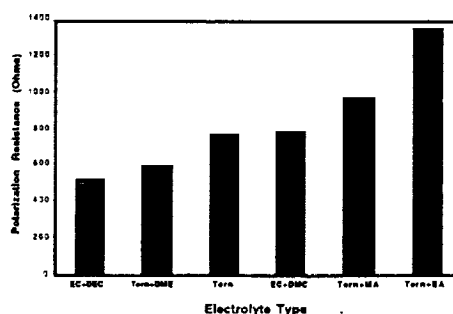


Fig. 10 Linear polarization resistance calculated from DC micropolarization plots of graphite electrodes with different electrolytes at room temperature.

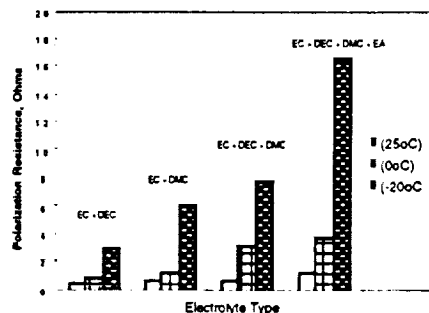


Fig. 11 Polarization resistance of graphite electrodes in contact with EC-based electrolytes of different types as a function of temperature.

### Low Temperature Discharge Capacity

After performing the electrochemical measurements described above, the discharge capacities were determined for the various cells under similar conditions. As shown in Fig. 12, the delivered capacities at  $-20^{\circ}\text{C}$  (25 mA current to 1.5 V cut-off vs.  $\text{Li/Li}^+$ ) correlate well with the results obtained with the DC micropolarization techniques. Due to the high polarization resistance observed at graphite electrodes in contact with MA or EA-containing electrolytes the delivered capacities were lower than that of the ternary carbonate mixture or the DME-containing electrolyte. Although differences are anticipated when these electrolytes are evaluated in experimental or prototype  $\text{LiCoO}_2$ -carbon cells due to cell design, pack tightness, and electrolyte volume, the observed trends should be consistent.

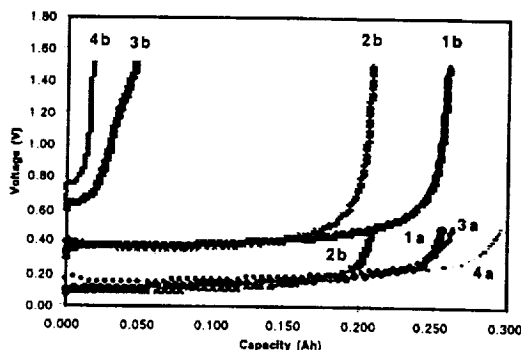


Fig. 12 Discharge curves of graphite electrodes in different electrolytes (1=EC+DEC+DMC, 2=EC+DEC+DMC+DME, 3=EC+DEC+DMC+EA, and 4=EC+DEC+DMC+MA) at different temperatures (A= $25^{\circ}\text{C}$ , B= $-20^{\circ}\text{C}$ ).

### Conclusions

A number of EC-based electrolytes with improved low temperature conductivity have been identified. These electrolytes are based on ternary mixtures of organic carbonates to which solvents possessing low viscosity and low melting points are added, such as, MA, EA, and DME. The compatibility of these electrolytes with graphite anode materials was assessed in lithium-graphite half-cells using various electrochemical techniques. Although some cells incorporating

these highly conducting electrolytes display low irreversible capacity losses during the formation cycles, such as with MA and EA, AC impedance and DC micro polarization methods have shown that these cells have high polarization and charge transfer resistance. Thus, the benefits of the highly conducting medium is offset by the poor  $\text{Li}^+$  intercalation-deintercalation kinetics of the graphite electrodes produced by the nature of the interfacial films.

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